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ROLE OF CHAR DURING REBURNING OF NITROGEN OXIDES

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ABSTRACT

The investigation of this quarter focuses on the rates of NO reactions with chars in various gaseous environments. The results have revealed significant insights into the NO reduction mechanisms on char surface, particularly when the oxidants, O_2 and CO_2 , are introduced into the feed. Indeed, evidences suggest that the formation of stable oxygen complexes is the major cause of difference in NO reactivity on chars of different origins.

The oxidants retard the reactivity of char derived from the bituminous coal more seriously than they affect the char derived from lignite. Furthermore, additions of these oxidants into the reacting stream produce additional yields of CO and CO_2 during NO reaction with lignite char, suggesting gasification of carbon from lignite char. No excess CO and CO_2 were observed when the bituminous coal char was used. These yields of CO and CO_2 also imply that desorption of stable surface oxygen complex is a rate-limiting step which may be catalyzed by the mineral matters during reactions involving lignite char.

Surface area evaluated by CO_2 and Dubinin-Radushkevich (D-R) equation is not a normalization factor of char reactivity during reburning. In the absence of oxidants, the bituminous coal char shows drastic increase in activation energy at about 950 °C indicating transition of desorption to adsorption controlled mechanisms. When CO_2 is introduced, the transition temperature increases. When oxygen is also added, no such transition is observed up to 1100 °C. Lignite char reactivity increases smoothly over the temperature range 800 to 1100 °C.

It is also observed that char reactivity decreases with increasing pyrolysis temperature which may be caused by closure of pores due to graphitization. The rate of NO reduction on the Pittsburgh #8 coal char is in good accord with that of a West Virginia coal char reported by De Soete (1980).

I. INTRODUCTION

The regulations established by the Clean Air Act Amendments of 1990 in the United States mean that a single NO_x control technology is not likely to be sufficient for boilers in the ozone non-attainment areas. Reburning is an emerging three-stage combustion technology designed for the reduction of NO by introducing a small amount of reburning fuel above the primary flame where the majority of NO is chemically reduced to nitrogen in this fuel rich environment. The concept of reburning was first introduced by Wendt *et al.* (1973). Tests on a full-scale boiler at Mitsubishi Heavy Industries (Takahashi *et al.*, 1983) resulted in over 50% NO_x reduction.

Coals, including lignites, are an economical source of carbon required for NO reduction in the fuel rich environment. Its effectiveness as a reburning fuel depends on two seemingly unfavorable factors. First, a fraction of the nitrogen in coal will be converted to NO in the reburning and burnout stages. Conversion of volatile nitrogen during reburning has been the objective of an earlier study of ours (Burch *et al.*, 1994). Second, while the homogeneous gas phase NO reduction in the fuel rich environment is relatively well understood (e.g., Miller and Bowman, 1989), the NO reburning by chars of diverse origin and history has not been the major objective of a systematic investigation.

Our previous studies of simulated reburning with reactors of two scales (Burch *et al.*, 1991a,b; 1994; Chen *et al.*, 1991) have demonstrated that lignites are more effective than methane. The two lignites tested were selected from Mississippi and North Dakota; both lignites have high contents of calcium. Initial screening with the North Dakota lignite indicated that the lignite char surface participates in heterogeneous/catalytic NO reduction to HCN, while lignite ash enhances catalytic HCN reduction to NH_3 . Both reactions are important in the overall NO reduction scheme. The effectiveness of lignite for NO reduction during reburning has recently been demonstrated in a

1.0 MMBtu/hr pilot scale test facility (Payne *et al.*, 1995).

Detailed kinetic analysis of homogeneous phase NO reduction in fuel rich environment indicates that the majority of NO is reduced by hydrocarbon radicals C, CH and CH₂ to HCN and amine radicals (NH₂) (Miller and Bowman, 1989). The amine radicals, in turn, can be converted to N₂ or NO. The yields of these desirable hydrocarbons radicals from lignite during reburning are not known. Nevertheless, coal and lignite produce only about 50% of the volatile carbons of that which methane produces at the same stoichiometry, which led to the speculation that the lignite char participates in considerable heterogeneous reactions with NO.

Although NO reburning by char has not been a major area of research, investigating the interactions of NO and carbonaceous materials has been the objective of a number of studies. An extensive review has been conducted by De Soete (1990). It has been shown that carbonaceous materials can be gasified by NO to form CO, CO₂ and N₂ (Bedjai *et al.*, 1958; Smith *et al.*, 1959; Furusawa *et al.*, 1980; Levy *et al.*, 1981; Chan *et al.*, 1983; Suuberg *et al.*, 1990; Teng *et al.*, 1992; Chu and Schmidt, 1993; Illan-Gomez *et al.*, 1993). The gasification reaction can be promoted by the addition of reducing agents, such as CO and H₂, and inhibited by O₂ when the CO₂/CO ratio is higher than one (De Soete, 1990). In addition to gasification, reaction of NO with CO on various surfaces, including char, ash and soot, can also be a major route of heterogeneous NO reduction mechanisms (De Soete, 1990). Catalytic decomposition of NO on various metallic oxides, some are common constituents in the lignite, has been reported by Winter (1971).

Huffman *et al.* (1990) reported that calcium is dispersed in coal macerals and is bonded to the oxygen anions. During combustion, the calcium present in lignite agglomerates, and eventually forms CaO and CaS. Recent lab-scale investigations of fluidized bed combustion (FBC) and circulating

FBC (CFBC) have shown that calcium sulfide (Hansen *et al.*, 1992), CaO (Allen, 1991; Hansen *et al.*, 1992; Hansen and Dam-Johansen, 1993; Shimizu *et al.*, 1993; Lin *et al.*, 1993) and Fe₂O₃ (Allen, 1991) serve as catalysts for NO reduction in various environments. While most of these researchers claimed that these catalysts enhanced the gasification or the conversion of NO + CO to form CO₂ and N₂, Lin *et al.* indicated that CO decreases the NH₃ conversion to NO. Lin *et al.* also claimed that NO may oxidize NH₃ to form nitrogen through homogeneous and heterogeneous mechanisms in FBC or CFBC. These char gasification and mineral-catalyzed reactions in reburning environment have not been fully investigated, but can certainly be enhanced by the highly porous nature of lignite char. The complexity of calcium-NO interactions has been demonstrated by infrared studies (Low and Yang, 1974; Allen, 1990).

The effects of calcium during oxidation of various solid carbonaceous materials has also been examined through a class of impregnation/ion-exchange techniques (Walker *et al.*, 1979; Radovic *et al.*, 1983; Hengel and Walker, 1984; Radovic *et al.*, 1985; and Levendis *et al.*, 1989). In a study of the catalytic effects of ion-exchange of lignite on char oxidation, Walker *et al.* found that the reactivity of various calcium-containing chars in air, CO₂ and water vapor increased linearly with increasing calcium. Radovic *et al.* discovered that the well-dispersed calcium oxide formed upon pyrolysis of lignites is a very efficient *in situ* catalyst for sulfur capture. The char reactivity decreases with the increasing severity of pyrolysis conditions which is probably due to CaO crystallite growth. Levendis *et al.* reported that carbon oxidation can be catalyzed by calcium up to 2 orders of magnitude.

Mild oxidation has been used to enhance the oxygen functional groups and the subsequent ion-exchange capability of carbonaceous materials (Chang *et al.*, 1986). Following the same concept,

Bartholomew *et al.* (1991) and Gopalakrishnan *et al.* (1994) produced char in the presence of oxygen and used the same ion-exchange/impregnation procedure discussed above. Their results indicate significant catalytic effects: up to a 160-fold increase for CaCO_3 catalysis, a 290-fold increase for CaSO_4 , and up to 2700 times for CaO .

While most of the studies in the literature have been centered around the Ca-catalyzed char oxidation by oxygen, Wojtowicz *et al.* (1991) reported that oxidation of a peat char by N_2O during fluidized bed combustion can be catalyzed by impregnating the char with CaO . Recently, Illan-Gomez *et al.* (1995) reported that calcium catalyzes NO-carbon reaction at 300 to 600 °C through a mechanism that is consistent with the formation of intermediate $\text{CaO}(\text{O})$ surface species.

The primary objectives of this study are to investigate the extend and to improve the understanding of heterogeneous NO reduction mechanisms during reburning with coal and lignite. The extend of heterogeneous mechanisms of NO reduction on lignite char has been demonstrated in the first year of this project (Chen and Ma, 1995). During this quarter, we focuses on the rates of NO reactions with chars in various gaseous environments.

II. WORK ACCOMPLISHED

The detailed flow reactor system for reburning and experimental procedure have been discussed by Burch *et al.* (1991a,b). The detailed char preparation procedure has been documented in our sixth quarterly report (Chen *et al.*, 1995a).

A. Measurements of the Surface Fractal Dimension

The BET-surface areas of nine samples were measured with nitrogen (N_2) and argon (Ar) as

the adsorbates at a temperature of 77 K. Measurements were carried out under six different relative pressures, P/P_0 , with the multi-point method. The P/P_0 ranging from 0.05 to 0.30 was within the region of the adsorption isotherm. Each P/P_0 leads to the weight of gas, W , adsorbed on the sample. The surface area of each sample has been recovered from the Brunauer-Emmett-Teller (BET) equation. The results are summarized in Table 1.

Additional measurements were carried out with carbon dioxide (CO_2) as the adsorbate at a temperature of 273 K. The P/P_0 ranging from 0.001 to 0.010 was within the region of the adsorption isotherm. The P/P_0 is small compared to that of the above measurements because the adsorbate saturation vapor pressure, P_0 , at 273 K is much larger than the atmospheric pressure. Measurements were carried out under eleven different levels of P/P_0 with the multi-point method. The surface area of each sample has been estimated with the BET equations. Furthermore, the micro pore volume and micro pore surface area of each sample have been calculated with the Dubinin-Radushkevich (D-R) equation (see, e.g., Lowell, 1979). Dubinin and Radushkevich (1947) postulated that the fraction of the adsorption volume, V , occupied by a liquid adsorbate at various adsorption potentials, E , can be expressed as a Gaussian function as

$$V = V_0 e^{-K(E/\beta)^2} \quad (1)$$

where V_0 is the adsorption volume of a reference liquid adsorbate; K , a constant related to the shape of the pore size distribution; and β , an affinity coefficient relating E to that of the reference adsorbate, E_0 , or

$$\beta = \frac{E}{E_0} \quad (2)$$

When the adsorbate is in the liquid state, the adsorption potential is given by

$$E = RT \left[\ln \frac{P_0}{P} \right] \quad (3)$$

If the above expression is substituted into Eq. 1, then

$$V = V_0 e^{-K \left[\frac{RT}{\beta} \ln \frac{P_0}{P} \right]^2} \quad (4)$$

or

$$\log V = \log V_0 - k \left[\log \frac{P_0}{P} \right]^2 \quad (5)$$

where

$$k = 2.303 K \left[\frac{RT}{\beta} \right]^2 \quad (6)$$

The micro volume is recovered from the intercept of a plot of $\log V$ against $[\log P_0/P]^2$. The results are summarized in Table 2.

B. Implications of Surface Reaction Mechanisms from CO₂ Surface Areas

Resorting to our previous reburning data, a first level kinetic analysis, and BET N₂ surface area, we concluded (Chen and Ma, 1995) that surface area alone is not able to contribute to the high conversion observed from reburning with lignite char, and chars of different origins seem to follow different mechanisms or to have different controlling steps in the overall reaction scheme. It is known that the N₂ at 77 K in BET measurement cannot penetrate into the micropores of chars and activated carbons (Mahajan and Walker, 1978; Yang, 1987). Alternatively, adsorption potential has been

estimated based on capillary condensation of adsorbate, such as the Dubinin-Radushkevich (D-R) equation (Mahajan and Walker, 1978; Yang, 1987). Our analysis with the D-R equation and CO₂ as the adsorbate, surface areas of chars after pyrolysis are 307.5 and 299.6 m²/g for chars derived from bituminous coal and Mississippi lignite, respectively (see Table 2). Surface areas of chars after reburning at SR=0.9 decrease to 228.5 and 199.9 m²/g for chars derived from bituminous coal and Mississippi lignite, respectively (see Table 2). Since the difference in CO₂ surface areas between the two chars is not as large as that of the N₂ surface areas, the conclusions about the impacts of factors other than surface area remain valid.

C. Rates of NO Reactions with Chars

1. Experiments

The experimental work conducted in this quarter focused on the effects of oxidants, CO₂ and O₂, and the effects of pyrolysis temperature on NO reduction. To study the effects of CO₂ and pyrolysis temperature, four series of experiments were conducted, three series were with the char derived from the Pittsburgh #8 coal and one series with the char derived from Mississippi lignite. NO reuction rates were calculated based on exit NO concentrations these five series of experiments.

The chars have been prepared during this quarter by pyrolysis in nitrogen at two gas temperatures, 950 and 1100 °C (1100 and 1150 °C set temperatures, respectively). The three series of experiments with chars derived from Pittsburgh #8 coal were conducted with 1) low temperature char without any oxidant, 2) high temperature char without oxidants, and, 3) high temperature char with CO₂. The experiments with char derived from lignite was conducted with high temperature char with CO₂. The NO/char experiments were conducted over the gas temperature range from 800 to

1100 °C with the same inlet NO concentration, 1000 ppm, residence time, 0.2 s, and a small variation in char feeding rate. The feed gas was balanced by He. Char feeding rate varied from 0.0325 to 0.0640 g/min. These char feeding rates corresponded to those used in reburning at $SR \approx 0.93$. Since the lignite char contains high level of mineral matters (about 50 %), the lignite char feeding rate is considerably higher than the feeding rate of bituminous coal char at the same SR. Details description of the flow reactor system and experimental procedure can be found in our first, sixth, and seventh quarterly reports (Chen *et al.*, 1994, 1995a, 1995b).

To further the study the effects of oxygen on char activity, six runs with different feed compositions have been conducted, three for each char: 1) NO+char, 2) NO+char+CO₂, and, 3) NO+char+CO₂+O₂. The gas composition for these experiments are consistent with those in the reburning environment, i.e., 1000 ppm NO, 16.8 % CO₂, and 1.98 % O₂. Char feeding rates correspond to those used at reburning stoichiometric ratio 0.93. Temperature and residence time were 1000 °C and 0.2 s, respectively.

2. Results and Discussion

a. Reaction during Heat-up and Cooling

During the last quarter, the estimated NO reduction rates were found higher than those reviewed by De Soete (1990). It was concluded that surface area measurement with BET in nitrogen, and reaction taking place during heatup and cooling periods may have caused the discrepancies. Corrective actions have been taken during this quarter. The effects of surface area measured by CO₂ and D-R equation have been discussed in the sections II.A and II.B. The extents of reactions during heatup and cooling will be discussed below.

The gas mixture enters the tubular reactor with a flowrate 2000 cm³/min at 25 °C. The cross section area of the tube is 2.865 cm². Assuming the gas is ideal, the gas residence time t in the heating up section can be expressed as a function of temperature and the traveled distance

$$dt = \frac{a}{G} dz = 25.62 \frac{1}{T} dz \quad (7)$$

where t is the gas residence time in the tubular reactor, in s

a is the cross section area of the reactor tube, in cm²

G is the gas volumetric flowrate, in cm³ s⁻¹

z is the longitudinal distance of gas traveled in the tubular reactor, in cm

T is the gas temperature in the tube, in °C.

The centerline temperature measurements were taken using a 0.32 cm o.d. sheathed but unshielded thermocouple. Due to high radiation from the walls, the temperature profiles obtained by this method are more representative of the wall temperature than the mean gas temperature at any given location. Using property data for the simulated flue gas composition and the method of Sellars *et al.* (1956) the maximum gas temperature is estimated to be 50°C lower than the maximum wall temperature and to be maintained for only 10 cm of the furnace length. The estimated average gas temperature and reaction time for this 10-cm zone are the basis for the data analysis presented in the last quarter. During the heating up period, the estimated temperature profile increases almost linearly with respect to z . Specifically, gas temperature increases from 700 to 1100 °C in 11.9 cm, thus, the heating rate can be written as

$$\frac{dT}{dz} = 33.51 \text{ } ^\circ\text{C cm}^{-1} \quad (8)$$

Substituting Eq. 8 into Eq. 7, we obtain

$$dt = \frac{0.765}{T} dT \quad (9)$$

For the cooling section, the gas temperature decreases along the tube length with the same rate, thus,

$$dt = - \frac{0.765}{T} dT \quad (10)$$

Assuming NO reduction follows a first order kinetics, material balance of a plug flow tubular reactor gives (Chen *et al.*, 1995b)

$$\frac{dP_{NO}}{P_{NO}} = \frac{-k A P_{NO, In} dW}{F_{NO, In}} \quad (11)$$

where: P_{NO} is the partial pressure of NO, in atm,

k is the Arrhenius' rate of NO reduction, in moles (s)⁻¹ (m)⁻² (atm)⁻¹.

A is the specific, internal surface area of char, in m²(g)⁻¹

W is the char weight in the reaction zone, in g

F_{NO} is the molar flowrate of NO, in moles s⁻¹.

Assuming the gas follows ideal gas law, F_{NO} can be expressed as

$$F_{NO, In} = \frac{P_{NO, In}}{P} \frac{v}{2.445 \times 10^4} \quad (12)$$

where v is the total inlet volumetric flowrate at 25 °C and P is the total pressure, 1 atm. The char weight, dW , in Eq. 11 can be expressed in terms of char feeding rate W_1

$$dW = W_1 dt \quad (13)$$

where W_1 is in $g s^{-1}$. The NO reduction rate, k , can be written as in Arrhenius form

$$k = k_0 \exp \left(\frac{-E_a}{R T} \right) \quad (14)$$

where k_0 and E_a are the preexponential factor and activation energy of NO reduction of char surface. Substituting Eqs. 9, 10, and 12 through 14 into Eq. 11, and integrating the resultant expression over the heating up, isothermal and cooling sections, we obtain the following expression

$$\begin{aligned} \ln(1 - X) = & \int 0.765 W_1 A k_0 \frac{1}{T} e^{-\frac{E_a}{RT}} dT - t_h W_1 A k_0 e^{-\frac{E_a}{RT}} \\ & - \int (-0.765) W_1 A k_0 \frac{1}{T} e^{-\frac{E_a}{RT}} dT \end{aligned} \quad (15)$$

where X is the NO conversion and t_h is gas residence time in the isothermal temperature region. The constants k_0 and E_a have been estimated by comparing the above equation with the experimentally acquired NO conversions at various temperatures on MathCad.

b. Effects of Char Origin, Char History, and CO₂ on NO Reduction

Figure 1 presents the three series of experiments conducted with the chars derived from the bituminous coal. The high temperature char, i.e., the char produced by pyrolysis at 1100 °C, has slight lower NO reduction efficiency than the low temperature char, i.e., the char produced by pyrolysis at 950 °C, during reburning at temperatures below 1100 °C. The difference in reactivity

between the chars diminishes above 1100 °C. The loss of reactivity of high temperature char could be caused by a number of reasons. First, it has been reported that pyrolysis of Pittsburgh #8 coal generates a small amount of H₂ (<0.4 wt % of as received coal) in the temperature range of 950 to 1100 °C (Howard, 1981), and this hydrogen yield may assist the removals of oxidants, CO₂ and O₂, and direct reduction of NO. Second, it has been speculated that the hydrogen complex formed on the partially devolatilized char, which also assist the removal of oxidants and NO (De Soete, 1990). Third, high temperature causes closures of pores due to a structure ordering of carbon, or graphitization (Radovic *et al.*, 1983; Sahu *et al.*, 1988; Wong *et al.*, 1995), and therefore reduces the contact area of char with NO. Our observation is certainly consistent with an earlier study of char reaction with air (Radovic *et al.*, 1983), in which char's reactivity was found to decrease with increasing pyrolysis severity, including temperature, heating rate, and holding time.

The two most striking and interesting observations about the bituminous coal char were that its reactivity increases drastically above 950 °C, and addition of CO₂ in the feed shifts this transition in char activity to higher temperature. The results of NO/char reaction were very consistent with similar results conducted during last quarter with an old Pittsburgh #8 sample. The shapes of the three curves in Figure 1 suggests that NO reduction on char surface follows at three different mechanisms or has different controlling steps over the temperature region 800 to 1100 °C. For example, higher temperature may activate the micropores which are not accessible to NO at low temperatures. It could also implies that the controlling step shifts from desorption to adsorption, which can be conceived by a Langmuir-Hinshelwood model involving adsorption of NO, and desorption of surface complex C-O to gaseous CO.



where C-O and C(N) represent chemisorbed oxygen complex and labile surface nitrogen, respectively.

Rearrangement of this reaction mechanisms give the expression for the global NO disappearance rate

$$-\frac{d(NO)}{dt} = \frac{k_1 k_2 P_{NO}}{k_1 P_{NO} + k_2} \quad (18)$$

When the reaction mechanisms are desorption-controlled, the expression above is reduced to a rate equation which is independent of NO concentration

$$-\frac{d(NO)}{dt} = k_2 \quad (19)$$

When the reaction mechanisms are shifted to adsorption-controlled at higher temperatures, the rate expression Eq. 18 is reduced to a rate equation which is first-order with respect to NO concentration

$$-\frac{d(NO)}{dt} = k_1 P_{NO} \quad (20)$$

It is known that the activation energy associate with adsorption is usually lower than desorption and transition from desorption-controlled to adsorption-controlled mechanisms is not likely under normal circumstances. Nevertheless, surface gasification involves highly structure-sensitive mechanisms (Lizzio, 1990), and such transition may take place if the micropores are penetrated by the reacting

gas at higher temperatures. Interestingly, the NO/bituminous coal char data collected from the last quarter with initial NO at 1000 and 400 ppm and temperatures below 950 °C seem to imply that the reaction is independent of NO concentration, and the mechanisms may indeed be desorption-controlled (Chen *et al.*, 1995b). Further investigations in this area are needed. The existence of multiple activation energies of NO reduction on chars derived from two low rank coals have been reported by Furusawa *et al.* (1980) and Chan (1983), though the transition temperatures in their studies were lower than what we observed.

Results shown in the Figure 1 also illustrate the retardation of NO surface activity by the presence of 16.8% of CO₂ above 950 °C. This observation suggests that CO₂ participates in forming surface oxygen-complex which leads to the reduction of active sites for NO adsorption and/or to the closure of micropores. This observation is consistent with the Langmuir-Hinselwood model postulated above.

Figure 2 illustrates the exit NO concentrations after NO reaction with CO₂ and char derived from the Mississippi lignite at 1100 °C. For comparison, results of NO reaction with char derived from Mississippi lignite at 950 °C (without CO₂) collected during last quarter were also included in Figure 2. In contrast to what we observed with the char derived from the bituminous coal, the lignite char does not display stiff change of NO concentration in the reaction conditions we investigated. Considering the high char feeding rate associated with the high temperature char experiments shown in Figure 2, the presence of CO₂ seems to inhibit NO reduction and the extent of its effects is discussed below.

Figure 3 presents the Arrhenius plot of rate of NO disappearance. As discussed in earlier parts of this report, the calculation procedure for this plot has been modified to include two

potentially important items: 1) CO₂ adsorption and D-R equation, instead of nitrogen adsorption and BET equation, are used for the estimation of internal surface areas, and, 2) the reactions during heating-up and cooling periods are included in the estimation of rates. The results reveals that the surface areas of the two low temperature chars derived from Pittsburgh #8 and Mississippi lignite measured by CO₂ adsorption are about 300 m²/g (Table 1), which are much higher than surface areas measured by BET in nitrogen reported in the last quarter (Chen *et al.*, 1995b). These results significantly lowered the NO reduction rates, as presented in Figure 3. The extent of reaction taking place in the heating-up and cooling periods were found to be minimal, and, therefore, did not contribute significant change to the estimations of rate constants. The numerical values of rate constants are shown in Table 3.

Figure 3 shows that the estimated rates for Pittsburgh #8 coal char are in surprisingly good agreement with that of a West Virginia coal char reported by De Soete (1980), but they are slightly higher than those reported by Song (1978), Levy *et al.* (1981), and Chan (1983). Nevertheless, these range of variations are expected since char's reactivity strongly depends on its structure and constituents, and, char's structure, in turn, depends on its origin and history.

As expected, the rates of char derived from Pittsburgh #8 coal has large variations in the temperature range studied (Figure 3 and Table 3). This trend may be due to the penetration of reacting gas to the micropores, and therefore, transition of desorption-controlled to adsorption controlled mechanisms, which have been discussed above. The char derived from lignite reveals much smoother changes in reactivity over the same temperature range. This observation is in general agreement with those observed with carbon gasification. For example, it is often found that the global activation energy for gasification in O₂ decreases with increasing disorder in the carbon

structure (Radovic *et al.*, 1983). If the coalification is considered a slow graphitization process, coal's rank, in general, increases with its structure order.

A number of potentially significant observations can be stated when the reactivities of chars of two different origins are compared. First, at high temperatures and in the absence of CO_2 and O_2 , the reactivity of the bituminous coal char is comparable, or even higher than that of lignite char. Second, when 16.8 % (by volume) of CO_2 is introduced into the feed stream, the reactivities of bituminous coal char are affected more severely than those of lignite char are affected. Since the reburning stage also contains about 2 % (by volume) of O_2 , the effects of CO_2 discussed above inspired our study of O_2 effects, which is discussed in the next section.

c. Effects of O_2 and Char Origin on NO Reduction

As we have stated, the major objective of the current project is to elucidate the roles of chars during reburning and, specifically, the reasons of high reactivity of lignite char with NO during reburning observed in the previous project. The effects of CO_2 on the char reactivities discussed in the last section provoked our postulation that the major difference in coal reactivities in reburning may be caused by their differences in reactivities with oxidants, including CO_2 and O_2 . To further verify the hypothesis, three runs with different gas compositions are conducted for each of the two chars of different origins: 1) NO+char, 2) NO+char+ CO_2 , and, 3) NO+char+ CO_2 + O_2 . The compositions of these six experiments correspond to those used in reburning, and have been discussed in the experimental section of this report.

The data presented in Figure 4 have been generated from experiments with high temperature chars. For the two runs with oxidants, both CO_2 and O_2 , the exit NO concentrations are higher than

what we observed with the low temperature chars reported in the sixth quarterly report (Chen *et al.*, 1995a). These data strengthen the conclusion that char reactivity decreases with increasing pyrolysis severity.

Results presented in Figure 4 also suggest that the reactivity of the bituminous coal char is comparable or even higher than lignite char when CO_2 and O_2 are absent, and CO_2 and O_2 are more detrimental to the NO reduction with the bituminous coal char than to that with the lignite char. Interestingly, the char gasification literature has offered some helpful explanations to what we have observed here, particularly through the concepts of "stable oxides," "labile oxides," and "reactive surface area" which have been well documented by Laine *et al.* (1963), Lizzio (1990) and Radovic *et al.* (1991). In the study of gasification of carbon by N_2O , Strickland-Constable (1938) distinguished two types of surface oxides: 1) stable oxides, i.e., those C-O complex which accumulate on the surface and inhibit oxidation, and 2) labile oxides, i.e., those C(O) complex which have a shorter lifetime and are active in the combustion mechanisms. Lizzio (1990) and Radovic *et al.* (1991) developed temperature-programmed desorption techniques for the quantifications of both C-O and C(O) complexes. They concluded that the surface area occupied by the labile oxides, i.e., C(O), is a better normalization parameter of char reactivity and is called "reactive surface area (RSA)." Furthermore, Lizzio (1990) theorized that RSA increases with decreasing structure order during gasification. His hypothesis is consistent with our observation that lignite char, a carbonaceous material having lower structure order than the bituminous coal char, has a higher reactivity in our gasification environments involving NO.

Freund (1985) and Lizzio (1990) discovered that RSA is not single parameter governing the activity of demineralized lignite char impregnated with calcium. In their experiments, considerably

more CO evolved than expected in transient kinetics, i.e., the exponentially decay CO yields immediately after gasification with CO₂. They concluded that CaO acts as an efficient dissociation center, which contribute the decomposition of complexes of lower reactivity, i.e., the stable C-O complexes. Their observations and conclusions are certainly consistent with our findings in Figure 4 that: 1) desorption of surface C-O complexes is a controlling step when oxidants (CO₂ and O₂) are present in reburning with char, and, 2) minerals, such as CaO, in the lignite char enhance the decomposition of the otherwise stable C-O complexes. These mechanisms are likely the major contributors to the lignite reactivities during reburning observed earlier in our study.

d. Yields of Carbon Oxides and Oxygen Balance

Carbon monoxide and carbon dioxide are the principal products of NO/char reaction. Figures 5 and 6 illustrate the yields of these two components, in volume percentages, from the reaction of NO with the bituminous coal char and the lignite char, respectively. The molar CO/CO₂ ratio is higher than one under all test conditions. These figures also included the net yields of CO and CO₂ from experiments including both CO₂ and O₂ in the feed.

It is very interesting to note that there is no clear excess yields of CO or CO₂ when oxygen is added introduced in the feed containing bituminous coal char, Figure 5. Nevertheless, significant excess yields of CO or CO₂ are observed when oxygen is included in the feed containing lignite char, Figure 6. These observations suggest the gasification of lignite carbon by oxygen during reburning, however, gasification of the bituminous coal char does not take place under similar experimental conditions. Since oxygen clearly retards the NO reduction of the char surface, as shown Figure 4, our observations discussed above strengthen the conclusion that stable oxygen complexes form on

the bituminous coal char surface while CaO on lignite char surface accelerates the decomposition of these stable oxygen surface complexes. The runs with CO₂ only do not result in notable yields of gasified carbon from char. The oxygen conversions from NO to CO and CO₂ are presented in Figures 7 and 8 for the bituminous coal char and the lignite char, respectively. Although the data fluctuate, they vary around complete recoveries.

IV. WORK FORECAST

In the succeeding quarter, we will continue the measurements of the rates of NO/chars with sequential addition of CO₂ and oxygen. Data will be compared with a Langmuir adsorption/desorption/surface reaction model. The surface area of char collected will be measured by BET method and the rates of surface reaction will be corrected by fractal dimension of char.

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Table 1. Specific surface areas measured with nitrogen and argon as the adsorbates at a temperature of 77K.

ID	Sample Name	Nitrogen	Argon
No. 1	Mississippi lignite char	15.09 17.52	13.32 13.35
No. 2	Mississippi lignite ash/char	40.79 41.56	44.87 45.55
No. 3-1	Mississippi lignite char	67.52 63.42	35.43 33.25
No. 3-2	Mississippi lignite char/ash @ SR=0.70 1100°C	35.19 37.65	36.18 36.85
No. 3-3	Mississippi lignite char/ash @ SR=0.94 1100°C	51.86 51.04	34.29 33.96
No. 3-4	North Dakota lignite char	33.26 35.23	34.46 35.66
No. 3-5	North Dakota lignite char/ash 1100°C	43.12 44.68	47.36 48.34
No. 3-6	Pittsburgh #8 bituminous coal char	18.53 18.49	13.37 13.69
No. 3-7	Pittsburgh #8 bituminous coal char/ash	10.66 11.62	13.76 13.09

Table 2. Specific surface areas evaluated with the BET equation and the micro pore volumes and micro pore surface areas evaluated with the D-R equation: adsorbate CO₂, operating temperature 273 K.

ID	Sample Name	Surface area [m ² /g]	Micro pore volume [cc/g]	Micro pore surface area [m ² /g]
No. 1	Mississippi lignite char	124	0.076	209
No. 2	Mississippi lignite ash/char	38	0.024	66
No. 3-1	Mississippi lignite char	172 168	0.108 0.109	299 300
No. 3-2	Mississippi lignite char/ash @ SR=0.70 1100°C	114 117	0.075 0.070	206 193
No. 3-3	Mississippi lignite char/ash @ SR=0.94 1100°C	121	0.083	228
No. 3-4	North Dakota lignite char	200	0.147	406
No. 3-5	North Dakota lignite char/ash 1100°C	192	0.134	371
No. 3-6	Pittsburgh #8 bituminous coal char	158 146	0.115 0.108	317 298
No. 3-7	Pittsburgh #8 bituminous coal char/ash	128 115	0.080 0.085	222 235

Table 3. Summary of Arrhenius' constants obtained under various feed concentrations and from two different chars

	$k_o, 1/(s \cdot \text{mole} \cdot \text{m}^2 \cdot \text{atm})$	$E_a, \text{Kcal/mole}$
MS. lignite W/O CO_2	6.36641	14.99
MS. lignite W/ CO_2	4.21824	15.31
Pitt #8, low temp. char, W/O CO_2	0.052286	8.024
	2.05×10^6	49.75
	3.08×10^5	38.81
Pitt #8, high temp. char, W/O CO_2	0.09596	11.90
	4.521×10^{15}	103.40
	1.862×10^8	58.54
Pitt #8, high temp. char, W/ CO_2	0.0458	10.21
	6.467×10^{11}	83.87
	1.615×10^6	49.92

* The feeding rate of Mississippi lignite char w/ CO_2 at $[\text{NO}]_{\text{in}} = 1000 \text{ ppm}$ is 0.064 g/min.
The feeding rate of Mississippi lignite char w/o CO_2 at $[\text{NO}]_{\text{in}} = 1000 \text{ ppm}$ is 0.0325 g/min.

† The feeding rate of Pitt #8 bituminous coal char at $[\text{NO}]_{\text{in}} = 1000 \text{ ppm}$ is 0.0446 g/min.

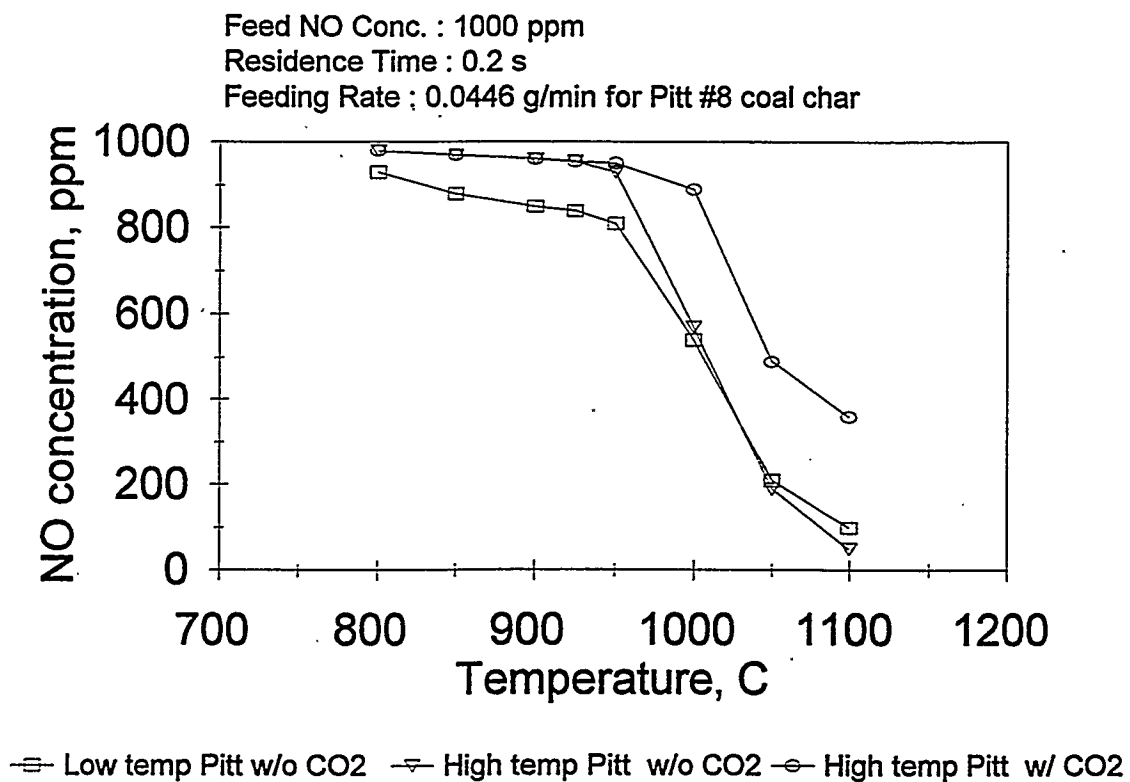


Figure 1. Exit NO concentrations from reburning with the Pittsburgh #8 coal char as functions of temperature, char pyrolysis temperature, and feed compositions. The NO to char ratio corresponds to that used in reburning at SR = 0.93.

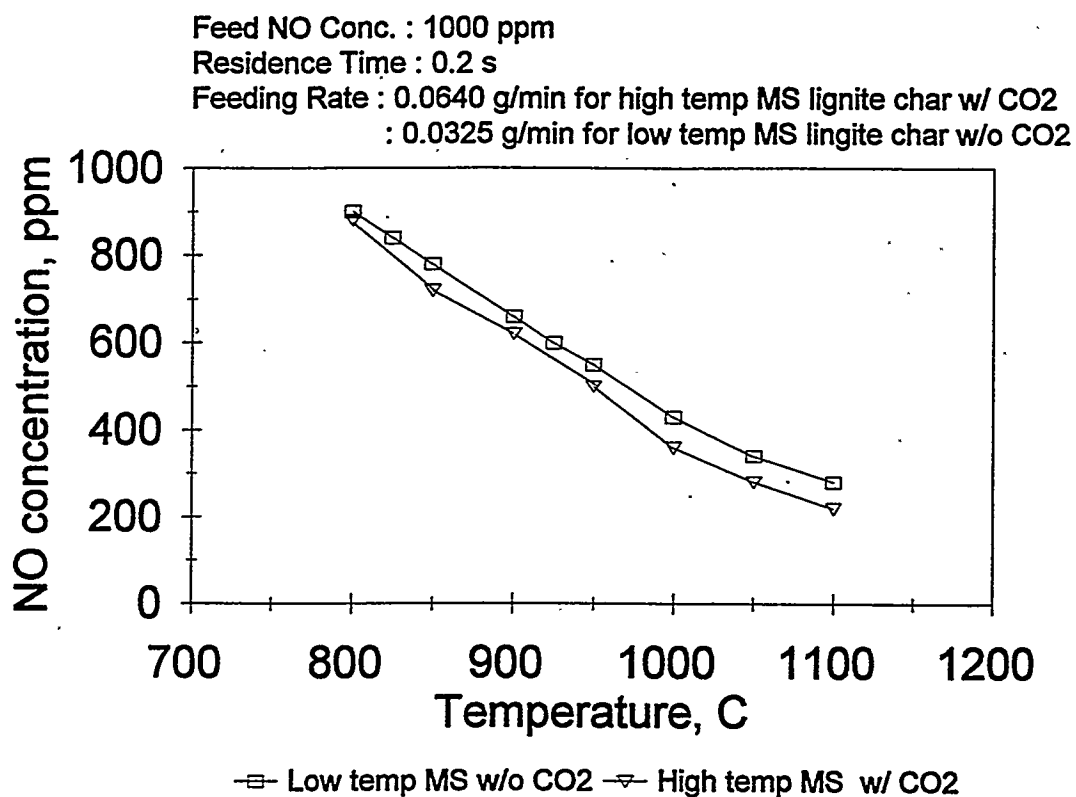


Figure 2. Exit NO concentrations from reburning with the Mississippi lignite as functions of temperature, char pyrolysis temperature, and feed compositions. The NO to char ratio for the runs with high char feeding rate corresponds to that used in reburning at SR = 0.93.

Feed NO Conc. : 1000 ppm
 Residence Time : 0.2 s
 Feeding Rate : 0.0446 g/min for Pitt #8 coal char
 0.0640 g/min for high temp MS lingite char w/ CO₂
 0.0325 g/min for low temp MS lignite char w/o CO₂

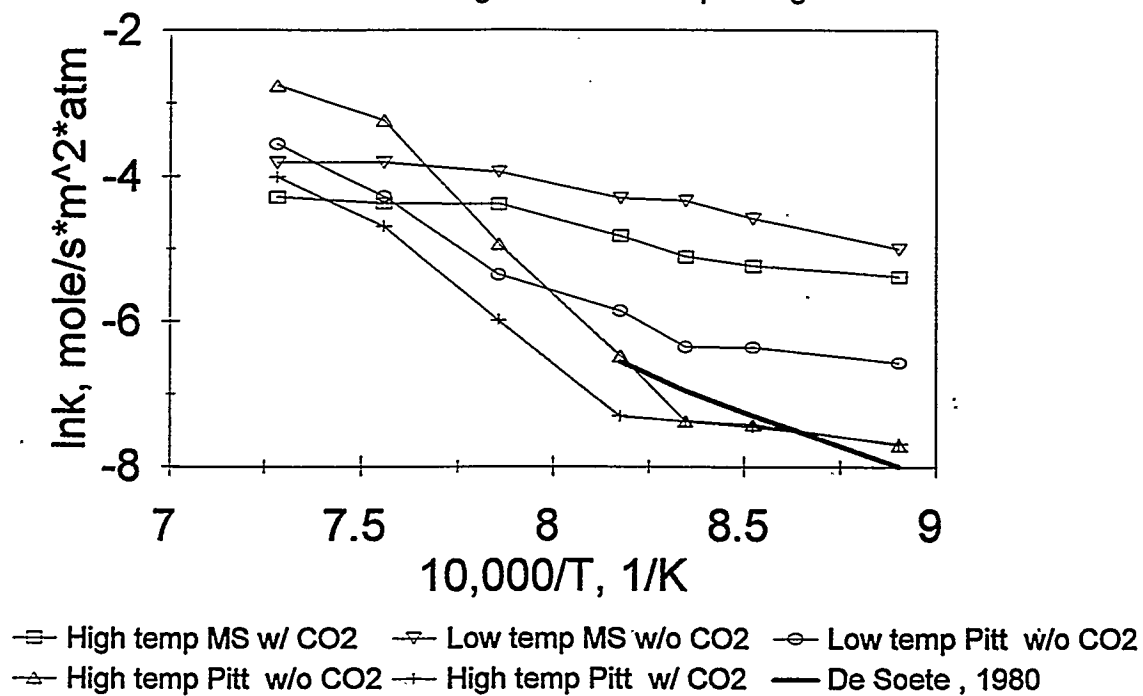


Figure 3. Arrhenius plots of NO reactions with chars of different origins and with different feed compositions. The solid line represents the rates reported by De Soete (1980) for a West Virginia bituminous coal.

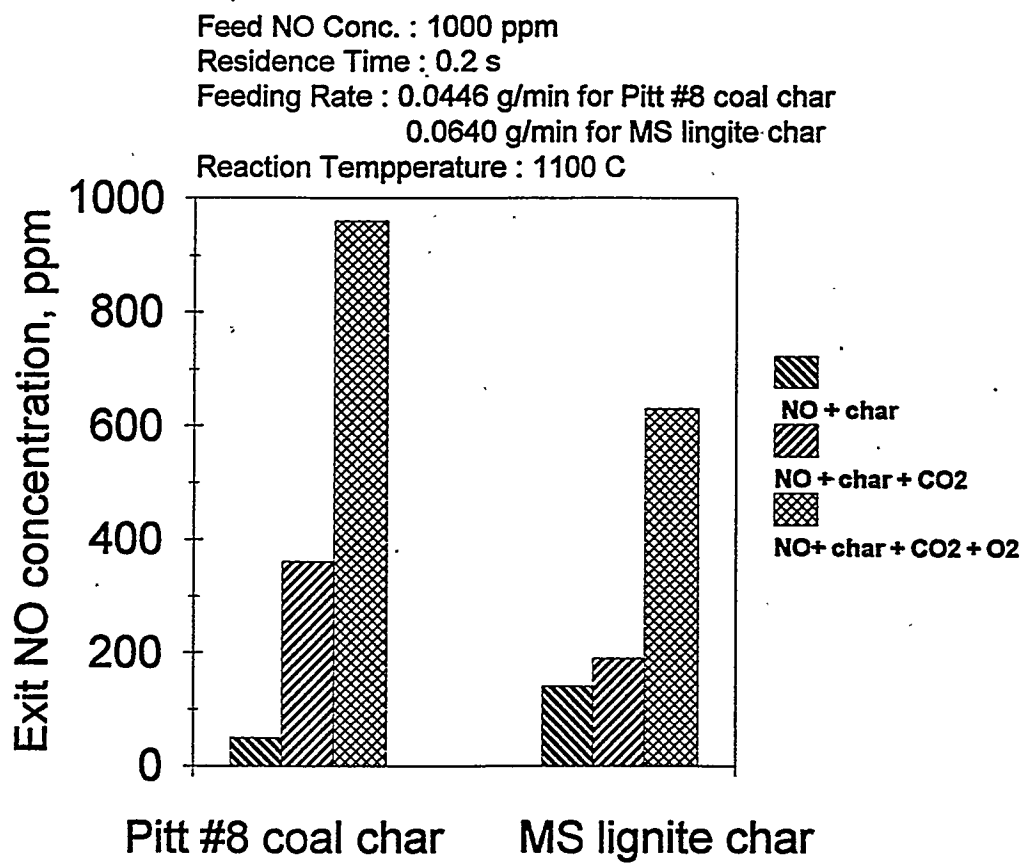


Figure 4. Effects of oxidants and char origins on exit NO concentrations. The NO to char ratio corresponds to that used in reburning at SR = 0.93.

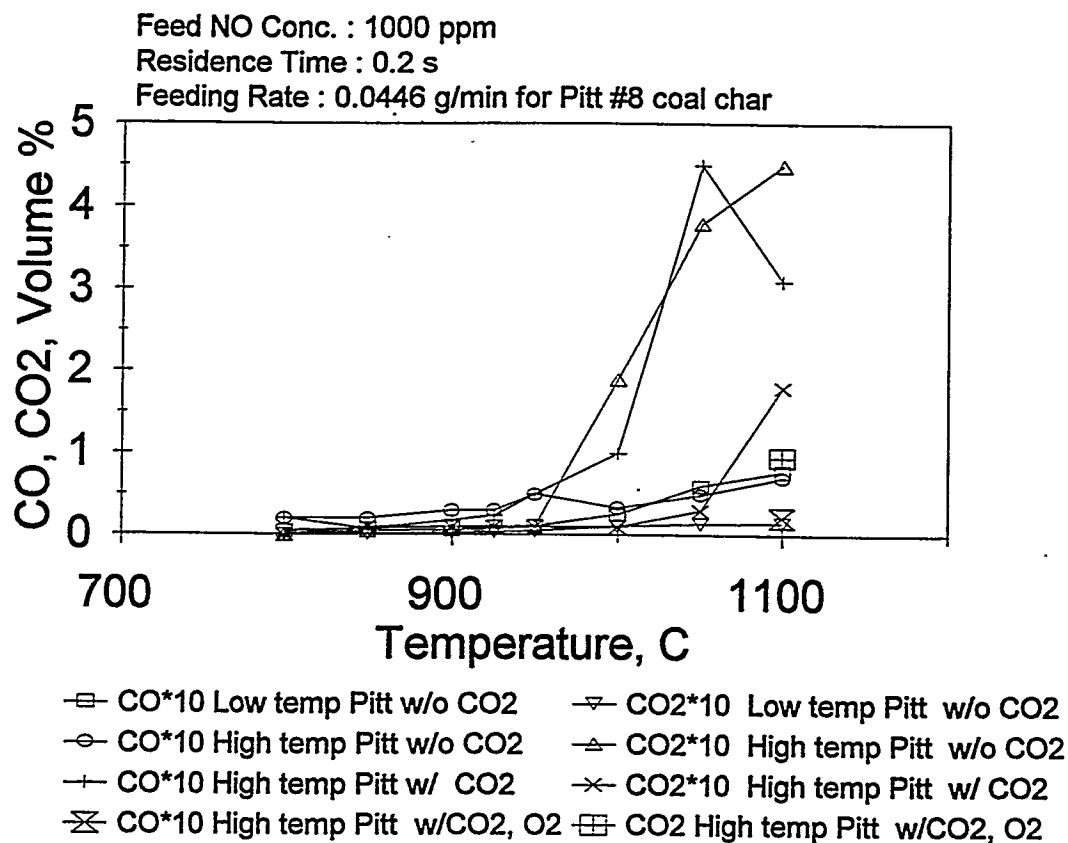


Figure 5. Yields of carbon oxides (in volume percentage) from the reactions of NO and Pittsburgh #8 coal char. No obvious gasification of char carbon is observed when oxidants are introduced.

Feed NO Conc. : 1000 ppm

Residence Time : 0.2 s

Feeding Rate : 0.0640 g/min for high temp MS lignite char w/ CO₂, W/ CO₂, O₂
0.0325 g/min for low temp MS lignite char w/o CO₂

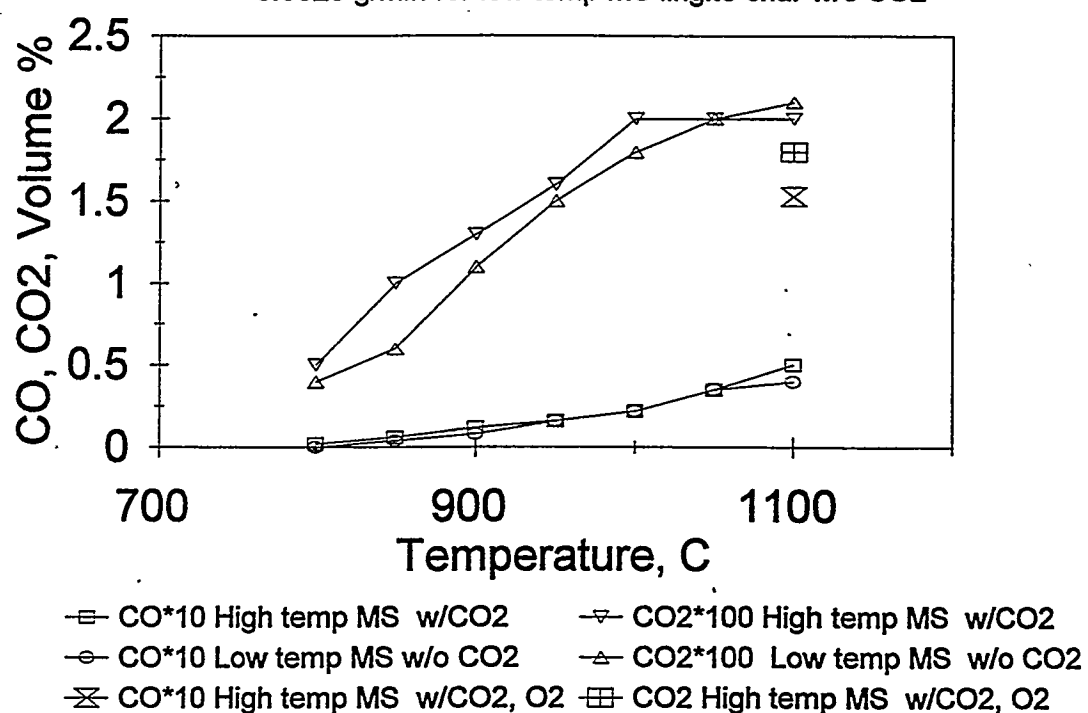


Figure 6. Yields of carbon oxides (in volume percentage) from the reactions of NO and the Mississippi lignite char. Obvious gasification of char carbon is observed when oxygen is introduced.

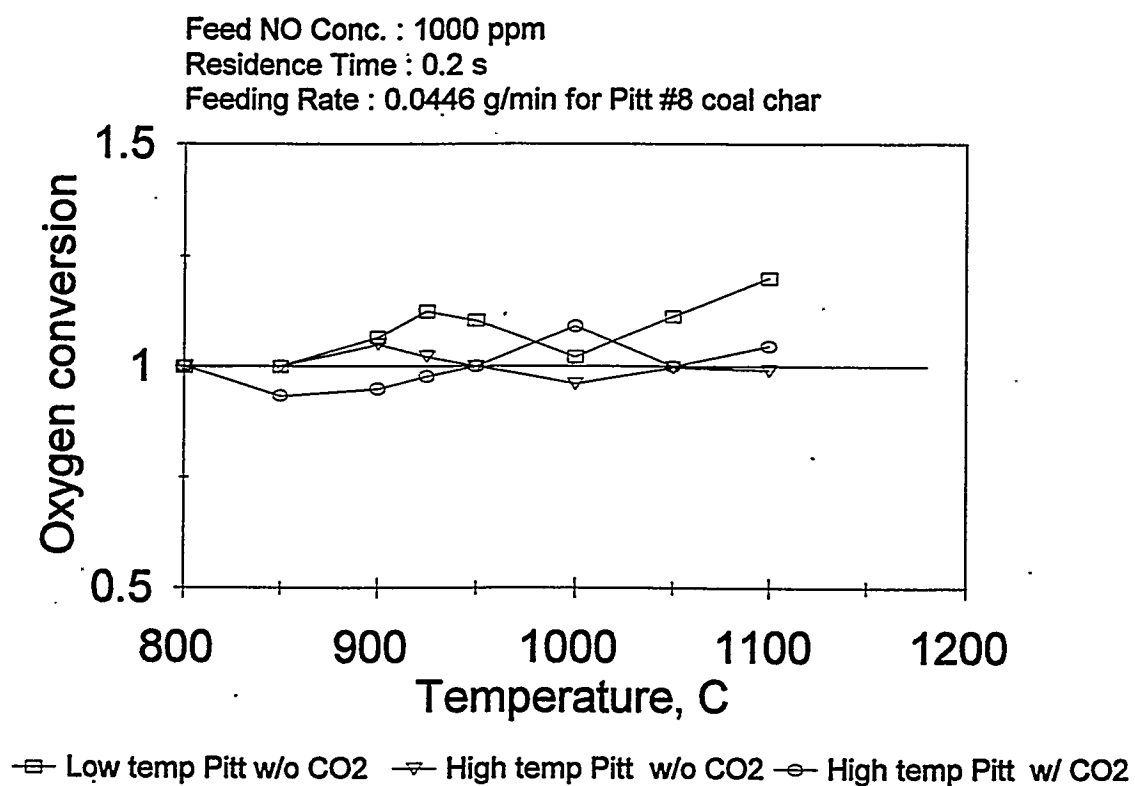


Figure 7. Conversions of oxygen of NO during reactions with Pittsburgh #8 coal chars and different feed gas compositions. Chars have been prepared under different temperatures.